EXHIBIT D

Publicly available information pertaining to DuPont’s Cementation Method:

1. U.S. Patent 4,375,986: Process for Treating Liquids Wastes Possessing A Strong Acidity (issued 1983)
2. U.S. Patent 5,076,850: Process for Treating Metal Chlorides (issued 1991)
3. EPA Site Report on Antioch Plant (1995)
4. Powerpoint presentation on Cementation created in collaboration of Professor Li of National Central University
5. Rong-Hsiang Lu Master Thesis on Cementation of Chloride Wastes (used at DuPont Kuan Yin Plant) (2005)
6. Abstract of thesis on ration of cement to waste

United States Patent [19]
Pichat

[11] **4,375,986**
[45] **Mar. 8, 1983**

[54] **PROCESS FOR TREATING LIQUIDS WASTES POSSESSING A STRONG ACIDITY**

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[58] **Field of Search** 106/85, 97, 117, 118, 106/DIG. 1

[56] **References Cited**

U.S. PATENT DOCUMENTS

3,720,609	3/1973	Smith et al.	106/109
4,028,130	6/1977	Webster et al.	106/DIG. 1
4,116,705	9/1978	Chappell	106/DIG. 1

OTHER PUBLICATIONS

Bond, M. S. et al. "Handbook of Environmental Control vol. IV: Wastewater: Treatment and Disposal", pp. 280, 286–287, 290 (1974).

Cassell, E. A. et al. "Solidification of Sludges with Portland Cement", *Journal of the Sanitary Engineering Division,* pp. 15–26, Feb., 19870.

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[57] **ABSTRACT**

Waste material having a pH not exceeding 2, and which have previously caused a serious disposal problem, are converted into stable, solid, useful, non-polluting products by first mixing the waste material with fly ash using about 30 to 260 parts of weight of ash for 100 parts of waste material, then neutralizing the resultant mixture using lime or calcium carbonate containing materials, next adding a calcium containing binder such as lime or Portland cement, and then solidifying the resultant mixture.

9 Claims, No Drawings

PROCESS FOR TREATING LIQUIDS WASTES POSSESSING A STRONG ACIDITY

BACKGROUND OF THE INVENTION

The present invention relates to the field of water-rich liquid wastes of various origins, such as industrial, farm and city wastes. It relates more particularly to a process making it possible to transform strong acidic wastes, having a pH of less than 2, into solid materials having great stability with respect to external agents, such as water. These liquid wastes possess a great retention power for polluting elements which are contained in these liquid wastes.

The increasing volume of wastes and residues, of all types, constitutes a problem which is of great concern to manufacturers and municipalities, particularly when one considers the fact that these wastes generally present great danger for the environment and for living beings. This is particularly a problem when these liquid wastes are strongly acidic.

Most often, the only acceptable solution from the economic and ecological viewpoint is to perform a treatment of these wastes, by physical or chemical means to effect solidification thereof. For this purpose, techniques have already been proposed which consist in mixing the waste slurry with suitable proportions of various ingredients, such as Portland cement, sodium silicate containing a setting agent such as lime, gypsum, calcium carbonate, a mixture of lime and pozzolana, gypsum or plaster in admixture with organic resins, or metallurgical slags carried in an alkaline medium in the presence of agents catalyzing the hydration of the slag.

These various processes rather often have offered interesting solutions to the solidification of muddy wastes but they resort to using treating products, as for example, Portland cement or similar products, the production of which involves high energy consumption. Further, they are not suitable in the particular case of treating liquid muds that are rich in water and very strongly acidic.

SUMMARY AND OBJECTS OF THE INVENTION

The present invention aims at solving these specific problems by using treating agents which are, per se, considered to be wastes and pose possible environmental problems if unused. Such treating agents are, however, suited for replacing, in great part, the hydraulic cements used heretofore for the solidification or petrification of wastes.

Because numerous countries are seeking to replace at least a part of petroleum with ground coal, thermal power plants produce increasingly larger amounts of wastes which are known as fly ash. These ashes, consisting of aluminosilicates, essentially contain silica (42 to 69%), alumina (21 to 49%), iron (3 to 13% in the form of $Fe_2O_3+TiO_2$), calcium (2 to 10% in the form of CaO), magnesium and a certain number of trace elements, and SO_3 (0.4 to 7%). These vitreous and crystallized ashes contain practically no free lime and relatively little bonded CaO, which distinguishes them from lignite ashes, which are not envisaged in the present invention and which exhibit hydraulic properties. As is known, coal ashes are pozzalanic, i.e., in the presence of, for example, lime, they agglomerate into a hard, compact and very stable material. Pozzalanic type mortars, moreover, have proved their stability since the Roman era.

Indeed, it has already been proposed to use fly ash in admixture with various products such as Portland cement, sodium silicate, and ground blast furnace slag to solidify muds. But, as stated above, the additions to these ashes of calorie-consuming products have been in undesirably large amounts and one of the purposes of the present invention is precisely to considerably reduce the proportions in these products of artificial types of hydraulic cement.

According to the novel process of the present invention, coal fly ashes are mixed with acidic liquid wastes. Subsequently, in one or more stages, the pasty mass is neutralized to a neutral pH and then a moderate amount of binder containing lime is added. The final mortar type product is then preferably deposited at the final site before setting.

Actually, one of the principal ideas in originating the present invention was to conceive a means to activate fly ashes of a pozzolanic type, the chemical reaction of which is very slow, as is known. It was found that contacting them with acidic products constituted an effective means to achieve this activation, even at external temperatures that can go down to 0° C. and less. Further, because of the further development of the above-described process, the difficult problem of eliminating toxic or potentially dangerous acidic wastes has been effectively solved.

The process of the present invention is actually totally different from certain other techniques whereby the wastes to be solidified are first neutralized, if they are acidic, with lime or similar product and mixed with other materials rich in sulfates and/or alumina, for example, fly ash. (See French Pat. No. 71.27555 or corresponding U.S. Pat. No. 3,720,609; French Pat. No. 74.40705 or corresponding U.S. Pat. No. 4,028,130; the article of E. A. Cassell et al, *J. of Sanitary Engineering Division Proceedings of American Society of Civil Engineers*, February 1970, pp. 15–26; U.S. Pat. No. 4,116,705). As will be shown below by comparative examples No. 13*a* and 13*b*, these techniques do not make it possible to obtain, at the start, a very fast solidification of highly active acidic liquid wastes which are envisaged by the invention, by using the same amounts of reagent, as in the invention herein.

DESCRIPTION OF PREFERRED EMBODIMENTS

The mixture of acidic wastes and fly ash is performed at regular pressure and temperature, for example, between 15° and 30° C., but it is possible to go down even to 0° C. and less, which is advantageous at the site. Preferably, the operation is performed with stirring, generally by using 30 to 260 parts by weight of ash for 100 parts of waste. The time of contact is a function of parameters, such as stirring, pH, granulometry and chemical composition of the ash, type of reactor used (thermally isolated or not), etc. In practice, this time varies between some dozens of seconds to several weeks but in the case of Vortex type stirring, it is generally between five and twenty minutes. Activation of the fly ash is shown, during mixing, by an exothermic reaction due to neutralization, particularly of the calcium compounds of the ash; the temperature can rise up to 100° C. During activation of the ash as a result of the reaction of the acidic waste with the constituents, such as aluminates, aluminoferrites, silicates, the acidic aqueous solu-

tion is enriched with ions. Examples of such ions are calcium, aluminum and silicates. The specific surface of the ash rapidly increases, for example, under the effect of a waste having an activity which corresponds to normal (N) sulfuric acid, an ash with an initial Blaine surface corresponding to 3,100 cm^2/g reaches a Blaine surface of 4,100 cm^2/g in a minute and in a day, with stirring, a Blaine surface of 7,600 cm^2/g. Finally, it was found that, during mixing, the pH, initially near 0, can increase to around a value of 4. Consequently, there is a substantial saving of neutralizing agent during the following phase of the process.

According to the second stage of the process of the present invention, the pasty mass is neutralized in the vicinity of neutrality (pH=7) with lime (quicklime or slaked lime) or a product containing these materials, such as ground limestone or residues having a calcium carbonate base. According to a variation of the process, it is possible to operate in several stages: for example, neutralization to about pH 4 (if this pH is not reached during initial mixing) using a calcium carbonate neutralizing agent and then continuing to attain a neutral pH using lime as neutralizer. Neutralization is accomplished by various precipitation reactions (for example, with added aluminates, silicates, borates, zincates, or phosphates) and also absorption, taking into account the considerable specific surfaces developed.

In the last stage of the process, a calcium binder is added, with stirring, to the pasty neutralized mass. As non-limiting examples of such binders, the following may be used, e.g. quicklime, residues from making quicklime or acetylene, natural hydraulic lime, Portland cement, blast furnace slag, slag cements, etc. This binder addition does not consist in simply coating the polluting elements but gives rise to complex absorption coprecipitation and complexing chemical-physical phenomena.

In practice, the weight ratio fly ash/$Ca(OH)_2$ is kept at least equal to 4 and can be increased up to 10 or 20, for example. For a given waste and operating temperature, solidification of the pasty mass by the binder is performed at a rate that is a function of the formulation and dosages used. In general the petrification time varies from a few hours to one or two days, the operation being checked by using a Vicat needle. At times, it is advantageous to add to the binder a silica sand and/or limestone, or an adjuvant as, for example, raw clay. Further, the reactions can be slowed down, if necessary by the addition of water, as for example, polluted water.

To practice the herein disclosed process, standard means and apparatus can be used. For example, mixing of the acidic waste and ash can be done in a mixer having a planetary movement driven by a turbine. Then the neutralizing reagents and the binder are added in the same apparatus accompanied by strong stirring. The resulting mixture, which has a viscosity of a mortar (for example of the $\frac{1}{3}$ Portland cement, $\frac{1}{3}$ water and $\frac{1}{3}$ sand type), can be subjected to extraction using a sliding trap or an extruder. Preferably, transport of the treated waste takes place during setting and before petrification. It is preferable that, during setting, the mass be compacted or packed to reduce the permeability of the material.

According to a variation of the process, the fly ash can be spread over a terrain, on which the acidic waste may be poured, and over which the neutralizing reagent or reagents and binder may be spread. Homogenization is performed by mixing the materials using a milling machine. The mixture is then compacted using vibrating rollers, which may be mounted an pneumatic tires, or by simply using a bulldozer. This technique can advantageously be used when the petrified material is obviously intended to remain on site.

The process of the invention makes it possible to treat all types of highly acidic liquid wastes, particularly having a pH higher than zero, of any origin, i.e., industrial, mining or urban wastes and of inorganic, organic or biological nature. These wastes may chemically contain metals, such as, for example, copper, iron, zinc, chromium, nickel, manganese, alkali metals, titanium, lead, vanadium, arsenic, antimony, or bismuth, anions such as chlorides, sulfates, sulfites, nitrates, fluorides, bromides, iodides, phosphates, cyanides, sulfides, borates, or thiocyanates, or organic compounds, such as protides, lipids, glucides, various hydrocarbons, etc. Finally, the wastes to be treated may be slightly radioactive.

The invention will be better understood from a detailed description of specific embodiments, cited by way of nonlimiting examples, which relate to the treatment of wastes of various compositions and sources.

ILLUSTRATIVE EXAMPLES

In the following examples, there were treated several types of strongly acidic liquid wastes, the composition of which is indicated in table 1 below, each element being expressed in mg/l$\times 10^3$ and the term COD (chemical oxygen demand) corresponding to the pollution of the waste.

TABLE 1

N° Waste	pH	Cu	Fe	Zn	Cr	Cd	Ni	Mn	So4	NO3	COD
I	0	2.1		2.6	175	0.05	1.1	0.5	410		575
II	0	0.22	0.90	0.40	0,35	0.001	0.5	0.005	165	115	550
III	0	9.4	81	7.6	1,6	0.038	0.65	0.65			
IV		95	175	1.75	35	2.2	85	27		1.5	75000

The origin of these wastes was as follows: chrome-plating shop for I, scouring of stainless steel for II, scouring of iron for III and dangerous industrial waste treatment plant for IV.

Unless otherwise indicated, the various ingredients used were of the following types:

coal fly ash with a composition: SiO_2—43%; Al_2O_3—34%; $Fe_2O_3+TiO_2$—8.5%; CaO—8.7%; MgO—1.9%; K_2O+Na_2O—1%; SiO_3—1.9%; loss in iron: 9%.

Portland cement: CPA 400 type, without additive.

Metallurgical quality lime

Blast furnace slag: Blaine fineness of about 4,000

Chalk dry content in $CaCO_3$ about 98% and Blaine fineness of 4000

Coarse limestone with dry $CaCO_3$ content of 89% and Blaine fineness of 9,000.

To evaluate the power of retention of the polluting elements in the products obtained according to the invention, a leaching test simulating the effect of stag-

nant water and the following mode of operation were used: samples of solid materials obtained according to the invention were introduced into open polyethylene pots, 7 cm high and with a 7 cm diameter (volume 150 ml). These containers were placed inside larger polyethylene pots, with an inner diameter of 8.5 cm, an outer diameter of 11 cm and a height of 14.5 cm; these latter pots were filled with distilled water. The unit was kept in the open air at a temperature on the order of 18° C. After at least a week, determinations were made, by known means, of the elements, particularly cations and anions, contained in the distilled water and which were not retained by the solid.

EXAMPLE 1

For about 10 minutes 100 g of waste No. I were stirred with 130 g of fly ash. The temperature, at the end of the mixing, reached 51° C. After neutralization to pH 7 by quicklime (about 6 g of CaO), it was mixed with 20 g of Portland cement.

By leaching tests for a week on a 28 day old sample of the resulting solid, the following results were obtained for the proportions of cations not retained by the petrified mass:

Cu, Fe, Zn, Cr, Cd, Ni, Mn: less than 0.1 mg/l (each)
COD: less than 20.

A crushing strength test on a sample of the same age, after 20 days of contact with distilled water, according to standard AFNOR P. 15-413 gave a crushing strength of 70 bars.

EXAMPLE 2

For about 10 minutes, 100 g of waste No. I were stirred with 140 g of fly ash. The temperature was 54° C. Neutralization to pH 7 with quicklime (5.67 g. of CaO) then followed, then 20 g of blast furnace slag were added.

After leaching under the same conditions as in example 1, the following elements (in mg/l) were found:

Cu, Fe, Zn, Cr. Cd. Ni, Mn—less that 0.1 (each)
SO_4^{--}—1.5; NO_3^{-}—6
COD—less than 20

Crushing strength (under same conditions as in example 1)—79 bars.

EXAMPLE 3

After stirring 100 g of waste No. I with 115 g of fly ash for 10 minutes, after which the temperature had risen to 45° C., neutralization was effected by adding quicklime (5.8 g of CaO), then 21 g of quicklime were added as a binder.

The results after leaching, as in example 1, were as follows (mg/l):

Cu, Fe, Zn, Cr, Ca, Ni, Mn—less than 0.1
$SO_4^{--}=0$; COD—less than 20
Crushing strength: 23 bars

EXAMPLE 4

For 10 minutes 100 g of acidic waste No. I were mixed with 122 g of fly ash, the mixture being cooled to maintain a temperature of about 22° C., Neutralization was effected to attain a pH of 7 by the addition of 61.5 g of chalk, then quicklime was incorporated in the mixture as a binder (21 g of CaO).

Under the same conditions as in example 1, the results after leaching were the following (mg/l):

Cu, Fe, Zn, Cr, Cd, Ni, Mn—less that 0.1 each
$SO_4^{--}=0$; $NO_3^{-}=10$
COD—about 20
Crushing strength—20 bars

EXAMPLE 5

Here 100 g of acidic waste No. II were mixed with 86 g of fly ash for 7 minutes. Neutralization was then effected by adding quicklime, then additional lime (a total of 22.3 g of CaO) was incorporated as a binder.

The results, after leaching as in example 1, were the following:

Cu, Fe, Zn, Cr, Cd, Ni, Mn—less than 0.1 mg/l each.
SO_4^{--}—130
Crushing strength—60 bars

EXAMPLE 6

For 30 minutes 100 g of Waste No. II were stirred with 40 g of fly ash. Neutralization was effected using 29.1 g of chalk, then a mixture of quicklime (11 g of CaO) and Portland cement (20 g) was added as a binder. After ten days of leaching, said cation contents remained less than 0.1 mg/l.

Crushing strength was 63 bars.

EXAMPLE 7

A mixture of 100 g of waste No. II was stirred with 101 g of fly ash for 12 minutes. After neutralization to pH 7 using quicklime, a mixture of 14.66 g of quicklime and 12.6 g of Portland cement was introduced as a binder.

After leaching of the sample under the same conditions as in example I, each of said cations was found in negligible amounts, less than 0.1 mg/l.

Crushing strength was 55 bars after keeping the sample under water for 20 days and 33 bars after keeping the sample in the atmosphere at 100% humidity and at a temperature of 8° C.

EXAMPLE 8

A type No. III aqueous waste was worked on by mixing 100 g of this waste with 120 g of fly ash for about twenty minutes. After neutralization, using quicklime (2 g), then the addition of quicklime (2 g) and Portland cement (16 g) as a binder, a petrified solid was obtained after two days, exhibiting approximately the same characteristics as in example 9 below.

Crushing strength was 18 bars.

EXAMPLE 9

For about 10 minutes 100 g of waste No. III was stirred with 21 g of fly ash. Neutralization was effected, and quicklime, totaling 28 g of CaO, was added as a binder.

After leaching the following amounts of cations (ml/g) not retained in the petrified solid were indentified:

Cu, Fe, Cr, Cd, Ni, Mn—less than 0.1 each.
Zn: 1.2.

The crushing strength for a sample of the same after 28 days of aging in contact with distilled water (standard AFNOR P 15-413) was 4 bars.

EXAMPLE 10

For 20 minutes 120 g of fly ash were made to react with 100 g of waste No. III, then neutralization was effected using natural hydraulic lime and the same product (lime) was added, totaling 20 g, as a binder.

After leaching less than 0.1 mg/l of each of the following cations were detected:

Cu, Fe, Zn, Cr, Cd, Ni, and Mn.

EXAMPLE 11

According to another mode of operation, a type No. II waste was left in contact with a third of its weight of fly ash for 48 hours without stirring. Then 100 g of the supernatant liquid phase was extracted and 72 g of fly ash were added, with stirring for 10 minutes. Neutralization was effected using 29.1 g of coarse limestone then several grams of quicklime was added, which functioned as a binder (for a total of 8 g of CaO).

After a week of leaching, it was not possible to detect more than 0.1 mg/l of the cations: Cu, Fe, Zn, Cr, Cd, Ni and Mn.

EXAMPLE 12

There were dissolved 30 g of Waste No. IV, which originally had a pH of 8, in 70 g of waste No. II. The resulting waste had a pH less than 0. This waste was made to react for 7 minutes with 110 g of fly ash. Then neutralization was effected using 3 g of CaO and then 18 g of Portland cement was added. The resulting petrified product had a crushing strength of 18 bars. The cation contents were less than 0.1 mg/l except for copper (2.9 mg/l). The COD had fallen to 650.

In all these examples, the solidification time of the treated waste masses, at regular temperature in an atmosphere of about 70% humidity, was always less than 12 hours except in the case of example No. 8 (two days).

EXAMPLE 13

Comparative tests were performed to show the notable differences in results from using, on the one hand, the prior art technique, above described, for treating wastes with a mixture containing a calcium binder and fly ash (test 13a) and, on the other hand, the process of the invention which in a preliminary phase treats the acidic waste with fly ash before the later stages of neutralization and the addition of binder (test 13b).

Test 13a: At the start 100 g of said type No. II waste, diluted once with water, were used. There were added 8.1 g of slaked lime, 18 g of quicklime (pH then went up to 14) and a dispersion of 180 g of fly ash, with stirring for 5 minutes. The temperature of the mixture reached 45° C. after this time.

The product was allowed to stand, then after 11 hours a penetration test was made with a Vicat needle, weighing 300 g and having a diameter of 4.5 mm. It was found that the needle went completely through the sample; the material therefore had not yet solidified.

After a new period of three and one half days a new penetration test was made with a Vicat needle of 300 g and a diameter of 1 mm. Again the needle went through the material.

After a new period of 8 days, the product was apparently well solidified and then the leaching test described above was made. After submersion in water for a period the sample actually disintegrated and therefore was not stable. Still the proportions of cations from the filtered product were analyzed and the following results were found (in mg/liter):

Cu—0.3; Fe—0.2; Zn—0.3; Cr—0.0; Cd—0.4; Ni—0.5.

Test 13b: To 100 g of the same waste as in test 13a were added 180 g of fly ash. The temperature rose to 62° C. and the reaction was allowed to go on for 60 minutes. It was found that the viscosity of the mixture increased considerably and that the pH reached about 3. After this 60 minute period, 8.1 g of slaked lime and 18 g of quicklime were added. A material, of a viscosity clearly greater than in test 13a, was obtained.

The same penetration tests with the Vicat needle as in test 13a were made after 11 hours and then after three and a half days. It was found that in both cases (4.5 mm, then 1 mm needle) no penetration occurred in the material which, from the 11 hour period, had solidified into an extremely hard mass.

Crushing strength, measured after 20 days of contact with distilled water, was 120 bars; therefore extremely high.

After leaching for a period of 3 weeks, the cations not retained by the petrified mass correspond to the following amounts (in mg/l):

Cu—0.2; Fe—0.1; Zn—0.1; Cr—0.0; Cd—0.0; Ni—0.2.

As can be seen from, these two tests 13a and 13b, only the process of the invention made it possible to rapidly obtain a solidified waste resistant to leaching and retaining its impurities; thus a material with excellent mechanical properties.

EXAMPLE 14

This example aims at showing the advantage, in certain cases, of replacing a part of the fly ash with a material such as clay.

To 100 g of waste No. II, diluted once with distilled water, 130 g of fly ash were added and allowed to react for about 7 minutes. Then 8.09 g of slaked lime and 13 g of quicklime were added, with the reaction mass being stirred for 5 minutes. Finally, 13 g of natural crude clay were incorporated in the mixture.

The mass solidified in about 24 hours and the crushing strength of the solid was 26 bars. After leaching, the amounts of cations detected in the wash water were the following:

Cu—0.2; Fe—0.2; Zn—0.1; Cr—0.0; Cd—0.4; Ni—0.4; Mn—0.4.

It will be obvious to those skilled in the art that various changes may be made without departing from the scope of the invention and the invention is not to be considered limited to what is described in the specification.

What is claimed is:

1. A process for treating liquid wastes diluted in water and possessing strong acidity (pH 2) to obtain stable solid materials that are non-polluting and resistant to water leaching, the process comprising the steps of:
 first, mixing the wastes with coal fly ash to form a pasty mass;
 then, neutralizing the pasty mass to neutral pH; and
 finally, adding a lime-containing substance to obtain a treated product.

2. Process according to claim 1 wherein said step of mixing the wastes and fly ash is performed at regular pressure and at a temperature ranging from below 0° C. to 100° C., using about 30 to 260 parts by weight of ash for 100 parts of the waste.

3. Process according to either claim 1 or 2 wherein said neutralizing step is effected using lime or products containing lime until a pH close to 7 is obtained.

4. Process according to claim 3 wherein said neutralizing step comprises first adding a product rich in calcium carbonate to attain a pH of about 4, and then adding lime to the mixture in an amount sufficient to obtain a pH of neutrality.

5. Process according to claim 4 wherein, in said neutralizing step, said product rich in calcium carbonate consists of a composition selected from the group consisting of ground chalk, ground limestone and residues derived from calcium carbonate base, and wherein said lime consists of either quicklime or slaked lime.

6. Process according to claim 1 wherein said lime containing substance used in said final adding step is selected from the group consisting of quicklime, slaked lime, Portland cement, lime manufacture wastes and blast furnace slags, and wherein the amounts of said lime-containing substance and fly ash are such that there is a ratio of fly ash to $Ca(OH)_2 \geqq 4$.

7. Process according to claim 1, wherein, after addition of said lime containing substance, raw clay is added to the mixture.

8. A process in accordance with claim 6 wherein said ratio of fly ash to $Ca(OH)_2$ approximates 10 or more.

9. A process in accordance with claim 1 wherein said treated product is deposited on a final disposal site before setting.

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United States Patent [19]
Eschborn, II et al.

[11] **Patent Number: 5,076,850**
[45] **Date of Patent: Dec. 31, 1991**

[54] **PROCESS FOR TREATING METAL CHLORIDES**

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[21] Appl. No.: **668,797**

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Related U.S. Application Data

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[52] **U.S. Cl.** **106/606**; 106/734; 106/287.35
[58] **Field of Search** 106/606, 734

[56] **References Cited**

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4,687,373 8/1987 Falk et al. 405/128

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Assistant Examiner—Chris Gallo
Attorney, Agent, or Firm—Robert B. Stevenson

[57] **ABSTRACT**

Process for making aggregate suitable for use as a road base material comprising:

(a) mixing metal chlorides with alkaline substance selected from the group consisting essentially of at least one cementitious material and optionally about 0.1-50%, based on the total weight of the alkaline substance, of at least one neutralizing agent, said mixing taking place in the presence of water in the amount of about 70-200 percent, based on the total weight of the alkaline substance,

(b) partially curing the product resulting from step (a), and

(c) agitating the product resulting from step (b) until aggregate is formed.

13 Claims, No Drawings

PROCESS FOR TREATING METAL CHLORIDES

This application is a continuation of application Ser. No. 07/425,402 filed 10-23-89 abandoned.

BACKGROUND OF THE INVENTION

This invention relates to an improved process for treating metal chlorides and especially such metal chlorides arising as byproducts from the chloride process for making TiO_2.

Large amounts of metal chlorides arise as byproducts from various industrial processes. For example, in the chloride process for making TiO_2, titanium bearing material or ore is chlorinated to produce $TiCl_4$ and other metal chloride byproducts. Subsequently, the $TiCl_4$ is separated from the byproducts and is oxidized to the desired TiO_2. The metal chloride byproducts are highly acidic and often contain iron chlorides as the major ingredient. While some of the byproducts can be used as a flocculant to treat waste water, large amounts must be disposed of by neutralization, land filling, deepwelling, etc.

Many processes have been proposed to neutralize and/or stabilize metal chloride byproducts. However, such processes appear to be deficient because they are both expensive and produce a product which still must be disposed of by landfill or other means.

The following information is provided which may be of interest in regard to this invention:

U.S. Pat. No. 4,229,399 discloses a process wherein solid mixtures of certain metal chlorides are mixed with certain alkaline substances followed by the addition of water. It is stated that the resulting product is substantially insoluble in water.

U.S. Pat. No. 4,375,986 discloses a process for neutralizing acidic waste material consisting of mixing the waste material with fly ash, neutralizing the resulting mixture with lime or other calcium containing materials, and adding a calcium containing binder such as lime or portland cement.

SUMMARY OF THE INVENTION

In accordance with this invention there is provided:

Process for making aggregate suitable for use as a road base material comprising:

(a) mixing metal chlorides with alkaline substance selected from the group consisting essentially of at least one cementitious material and optionally 0.1–50%, based on the total weight of the alkaline substance, of at least one neutralizing agent, said mixing taking place in the presence of water in the amount of about 70–250 percent, based on the total weight of the alkaline substance,

(b) partially curing the product resulting from step (a), and

(c) agitating the product resulting from step (b) until aggregate is formed.

It has been found that the process of this invention neutralizes and stabilizes metal chlorides so that they are resistant to leaching by water and are resistant to leaching as determined by current official tests of the U.S. Environmental Protection Agency and the State of California. Also, the product resulting from the process of this invention is suitable for and can be sold as high quality aggregate for road building. In contrast, the products from many prior art processes are only suitable for costly disposal in landfills.

Other advantages of the process of this invention are that the aggregate resulting therefrom (a) can exhibit greater strength than crushed rock road base, especially in layers of less than about 6–8 inches; (b) has a greater volume to weight ratio than most crushed rock and therefore will provide more road base per unit weight; and (c) can exhibit residual cementing action, i.e., when compacted, the aggregate can bind together and thus form a more cohesive mass, with good integrity.

DETAILED DESCRIPTION OF THE INVENTION:

Step (a)

In this step of the process of this invention, metal chlorides are mixed with an alkaline substance selected from the group consisting essentially of at least one cementitious material and optionally 0.1–50% of at least one neutralizing agent in the presence of water.

The metal chlorides preferably are in an aqueous solution and/or suspension. Suitable metal chlorides can be obtained as byproducts from various industrial processes. Examples include metal chloride byproducts from the manufacture of titanium dioxide by the chloride process, pickle liquor arising from the cleaning of iron, steel or other metals with hydrochloric acid, and metal chloride byproducts arising from various metal plating processes. This process is especially suitable for treating the metal chloride byproducts arising from the manufacture of titanium dioxide.

Suitable cementitious materials include hydraulic cement (including portland cement ASTM types I, IA, IP, IS, II, IIA, III, IIIA, IV, and V; aluminous cement; blast furnace slags; and mixtures thereof). Preferred are the foregoing ASTM portland cements, especially preferred are types I, IA, IP, IS, II, and IIA.

Suitable neutralizing agents include quick lime, residues from making quick lime or acetylene, lime, fly ash, soda ash, CaO, $Ca(OH)_2$, $CaCO_3$, and mixtures thereof. Generally, the neutralizing agent, if used, will be present in an amount of about 0.1–50%, preferably 0.1–25% and most preferably 0.1–10%, based on the total weight of the alkaline substance.

The use of the neutralizing agent is optional. It may be desirable to use some neutralizing agent because it often is less expensive than cementitious material. However, generally, use of the neutralizing agent can degrade the strength of the aggregate formed. Thus, the amount of neutralizing agent should be controlled so that the strength of the aggregate is within the desired range.

The water used in this step of the invention will generally be about 70–200 percent, preferably about 100–180 percent, more preferably about 130–150 percent, and most preferably about 140 percent based on the weight of alkaline substance. Note that the water can be added separately, included with the water contained in the metal chloride byproducts or both.

It has been found that lower density aggregates, with acceptable properties for road base material, are formed when a minimal amount of energy is used to carry out the mixing.

Generally, at least sufficient alkaline substance should be used to neutralize the metal chlorides and to provide the desired physical strength for the aggregate. For road base material, on a weight basis, this often will require at least about 2 parts alkaline substance per part of metal chloride.

Step (b)

In this step of the process of this invention, the product resulting from step (a) is partially cured. By "partially cured" it is meant that such product is allowed to cure for a sufficient time so that it is resistant to slump and flow, but it is not in a hardened mass which would be difficult to break into aggregates. Whether or not the product has sufficiently partially cured can be easily tested by withdrawing a small sample, agitating it (such as by mixing or stirring), and observing whether suitable aggregates are formed. Another suitable test is to determine whether or not a small sample can be crumbled by hand; if so, one can proceed to step (c).

Ordinarily, the partial curing will take place in about 4–24 hours. It generally is preferable during this step to shape the product resulting from step (a) into a compact mass to minimize evaporation of water. A suitable method for carrying out this step of the process is to deposit the product resulting from step (a) into a concrete holding basin or a vessel. Also, to minimize evaporation of water, the product being processed in this step of the invention can be covered. An alternative method for carrying out this step is to deposit the material onto a concrete pad or other suitable laydown area and optionally covering it with a waterproof membrane (such as a plastic sheet or tarpaulin).

Step (c)

In this step of the process of this invention, the product resulting from step (b) is agitated until aggregate is formed. Suitable methods for carrying out the agitation include: spreading and/or piling the material, mixing, shaking, vibrating, and combinations thereof. The concept involved in this step of the invention is that while curing continues to take place, the material is agitated so that aggregates are formed, rather than a hard, solid, compacted mass. Of course, to conserve energy, it is desirable to use the minimum amount of agitation necessary to produce the aggregates. For road base material, preferable aggregates often will have the consistency of fine sand, having agglomerates thereof dispersed throughout the sand. The agitation can be carried out continuously or intermittently. Intermittent agitation is preferred.

FINISHING OPERATIONS

After the aggregates are formed, it ordinarily is desirable to allow final curing to take place so that the aggregate has the desired amount of strength and integrity. This final curing ordinarily will be sufficiently complete within 1–4 weeks.

After the final curing, if desired, the aggregate can be subjected to screening, crushing, and moisture adjustment.

The aggregates made by the process of this invention can be used as base material for road building or in engineered fills where a quality structural material is desired.

EXAMPLE

The following example illustrates the operation of this invention. Unless otherwise indicated, all percentages are on a weight basis.

Metal chloride solution in the amount of 6000 pounds was placed in a rotary drum turning at 6 revolutions per minute. The metal chloride solution was a byproduct from a chloride process for producing TiO_2 pigment and had the following composition:

Ingredient	Percent
FeCl3	1.2
FeCl2	8.6
TiO_2	8.0
Coke	8.2
SiO2	0.8
TiOCl2	8.5
AlOCl	2.6
VOCl3	0.5
MnCl2	2.0
CrCl3	0.6
MgCl2	1.0
CaCl2	0.1
HCl	1.2
Cl- (arising from metal chlorides other than above)	1.3
Insolubles (other than above)	0.5
H2O	55.0
Total	100.0

While mixing was continued, 5000 pounds of water and 6000 pounds of ASTM Type-I portland cement were added.

The resulting material was then discharged to a concrete basin and shaped to minimize the surface area. After 12 hours, the material was removed from the basin with a front end loader and then spread out and piled. Subsequently, the material was spread out and repiled after 12 and 24 hours.

Afterwards, the material was allowed to cure for a week and subjected to screening, crushing, and moisture adjustment to produce a finished product.

The invention claimed is:

1. Process for making aggregate suitable for use as a road base material comprising:

(a) mixing metal chlorides with alkaline substance selected from the group consisting essentially of at least one cementitious material and optionally about 0.1–50%, based on the total weight of the alkaline substance, of at least one neutralizing agent, said mixing taking place in the presence of water in the amount of about 70–200 percent, based on the total weight of the alkaline substance,

(b) partially curing the product resulting from step (a),

(c) agitating the product resulting from step (b) until aggregate is formed and

(d) curing the product of step (c) until aggregate of the desired strength and integrity is formed.

2. The process of claim **1** wherein the alkaline substance is portland cement and the neutralizing agent is lime.

3. The process of claim **1** wherein the water is present in an amount of about 100–180 percent.

4. The process of claim **1** wherein the water is present in an amount of about 130–150 percent.

5. The process of claim **1** wherein the water is present in an amount of about 140 percent.

6. The process of claim **1** wherein the partial curing in step (b) is carried out for about 4–24 hours.

7. The process of claim **1** wherein the agitation in step (c) is carried out for at least about 12 hours.

8. The process of claim **1** wherein the agitation of step (c) is carried out for about 12–72 hours.

9. The process of claim **1** wherein the alkaline substance is portland cement, the neutralizing agent is lime, and the water is present in an amount of about 100–180 percent.

10. The process of claim **1** wherein the alkaline substance is portland cement, the neutralizing agent is lime, the water is present in an amount of about 100–180 percent, the partial curing in step (b) takes place for

about 4–24 hours, and the agitation in step (c) takes place for about at least 12 hours.

11. The process of claim **11** wherein the water is present in an amount of about 130–150 percent.

12. The process of any one of the preceding claims **1–11** wherein the metal chlorides are in aqueous form from a chloride process for making TiO_2.

13. Aggregate resulting from the process of any one of claims **1–11**.

* * * * *

Memorandum
To: Phase IV Supplemental Rulemaking RCRA Docket No. F-95-PH4AFFFFF
From: Van E. Housman
Subject: Site Visit Report - Wastes From the Production of Titanium Tetrachloride, DuPont Antioch CA Facility, July 31, 1995.
Date: November 13, 1995

The following individual were present on the site visit DuPont's facility. EPA HQ: Van Housman, Ron Brown; EPA Region 9: Dennis Geiser, Duong Nguyen, Jean Daniel; California DTSC: Vajie MotiaFord; DuPont: Dimitris Argyriou, Brian Coleman.

This facility is a major chemical manufacturing plant, producing chlorofluorohydocarbons, titanium pigments, and other products (see DTSC inspection report for further details).

Synthetic rutile, comprising 85% TiO_2, 12% FeO, and small amounts of aluminum and silicon, is received from Australia and South Africa in the form of crushed slag from smelting operations. The type of smelting that produced the rutile is not known. DuPont documents also refer to this as a "ilmenite-type ore" (see DuPont January 26, 1987 memo), which is reacted with chlorine in the presence of coke in a chlorinator vessel. Titanium tetrachloride and other metal chlorides are formed. Iron chloride waste acids are generate at the rate of approximately 30,000 tons per year and typically would be classified as hazardous because of corrosivity. This iron chloride acid waste, which previously was deepwell injected or landfilled on-site, is stored in a tank and then piped to a separate area for treatment. At the treatment area, the waste acids are mixed with Portland cement in an underground concrete pit (about 20 feet in diameter and several feet deep) to produce a material referred to as "Sierra-Crete". This mixing results in a vigorous exothermic reaction between $FeCl_3$ and $Ca(OH)_2$ to produce FeOOH and $CaCl_2$. The reaction has the physical appearance of boiling mud. The produced Sierra-Crete has a dirt- or soillike physical appearance.

The cost of producing Sierra Crete is approximately $80 per ton. DuPont sells Sierra Crete for $3 per ton to local companies for use as road base material. About 16,000 tons of Sierra Crete are stored on the ground at any one time.

Waste hydrochloric acid is generated by the reactors' scrubbing system. The hydrochloric acid is treated with sodium hydroxide to produce sodium chloride waste, which is discharged through a NPDES permit, and magnesium hydroxide which is landfilled on-site. The quantities of these wastes are not known.

The chlorinator vessel, where the rutile is reacted with chlorine gas, is cleaned every two years to remove impurities. Residues from the chlorinator bed are removed and sent to an off-site landfill. The location of this landfill, and quantities of waste shipped there, were not provided. According to DuPont, these residues do not fail the hazardous characteristic test.

Commodity Titanium and Titanium Dioxide

Waste Stream	**Nature of Operation**
Flotation Cells	Extraction/Beneficiation
Tailings	Extraction/Beneficiation
Spent Brine Treatment Filter Cake	Mineral Processing
FeCl Treatment Sludge	Mineral Processing
Waste Ferric Chloride	Mineral Processing
Finishing Scrap	Mineral Processing
Leach Liquor and Sponge Wash Water	Mineral Processing
Waste Non-Contact Cooling Water	Mineral Processing
Pickling Liquor and Wash Water	Mineral Processing
Scrap Detergent Wash Water	Mineral Processing
Scrap Milling Scrubber Water	Mineral Processing
Reduction Area Scrubber Water	Mineral Processing
Chlorination Off gas Scrubber Water	Mineral Processing
Chlorination Area -Vent Scrubber Water	Mineral Processing
Melt Cell Scrubber Water	Mineral Processing
Chlorine Liquefaction Scrubber Water	Mineral Processing
Chip Crushing Scrubber Water	Mineral Processing
Casting Crucible Contact Cooling Water	Mineral Processing
Smut from Mg Recovery	Mineral Processing
Spent Surface Impoundment Liquids	Mineral Processing
Spent Surface Impoundment Solids	Mineral Processing
$TiCl_4$ Purification Effluent	Mineral Processing
Spent Vanadium Oxychloride	Mineral Processing
Sodium Reduction Container Reconditioning Wash Water	Mineral Processing
Casting Crucible Wash Water	Mineral Processing
Waste Acids (Chloride process)	Mineral Processing
Waste Solids (Chloride process)	Mineral Processing
Waste Acids (Sulfate process)	Mineral Processing
Waste Solids (Sulfate process)	Mineral Processing
WWTP Liquid Effluent	Mineral Processing
WWTP Sludge/Solids	Mineral Processing

礦 尾 渣 水 洗 之 研 究

指導老師：李　　劍 教授

學　　生：陳 鈾 森

日　　期：12月26日

簡 報 大 綱

- 前言
- 文獻回顧
- 水洗設備與研究方法
- 預期結果
- 參考文獻

一、前　言(1/2)

- 由於台灣杜邦公司生產二氧化鈦衍生的副產品「礦尾渣」(KYC2)，為顆粒細、含氯量高及酸性的物質，現今處理方式為添加約三倍的水泥量拌合，凝結硬固後稱之為「鈦鐵礦氯化爐碴」，因鈦鐵礦氯化爐碴含氯量高，並不適用於鋼筋混凝土之構造物，初期只用於道路鋪面底層。
- 現今的道路鋪面的基底層中常埋設金屬管路，如自來水管或瓦斯管等，為避免金屬管路遭受鈦鐵礦氯化爐碴中氯離子的腐蝕，有必要對礦尾渣做適當的前處理，以降低礦尾渣中的氯離子含量。

前　言(2/2)

- 在前期的研究計畫中發現，藉水洗與添加適當的藥劑可大幅降低礦尾渣中的氯離子含量，得到接近規範的細粒料，達到最佳化的程度。
- 本研究擬針對將來不同的用途，分別以4000ppm和500ppm的氯離子含量為目標，探討適當的礦尾渣水洗除氯技術並做成本估算。研究擬分為小規模的程序試驗與較大規模的量產型試驗，水洗過程將分為中和、沉降、加藥、過濾等部份。

二、文 獻 回 顧

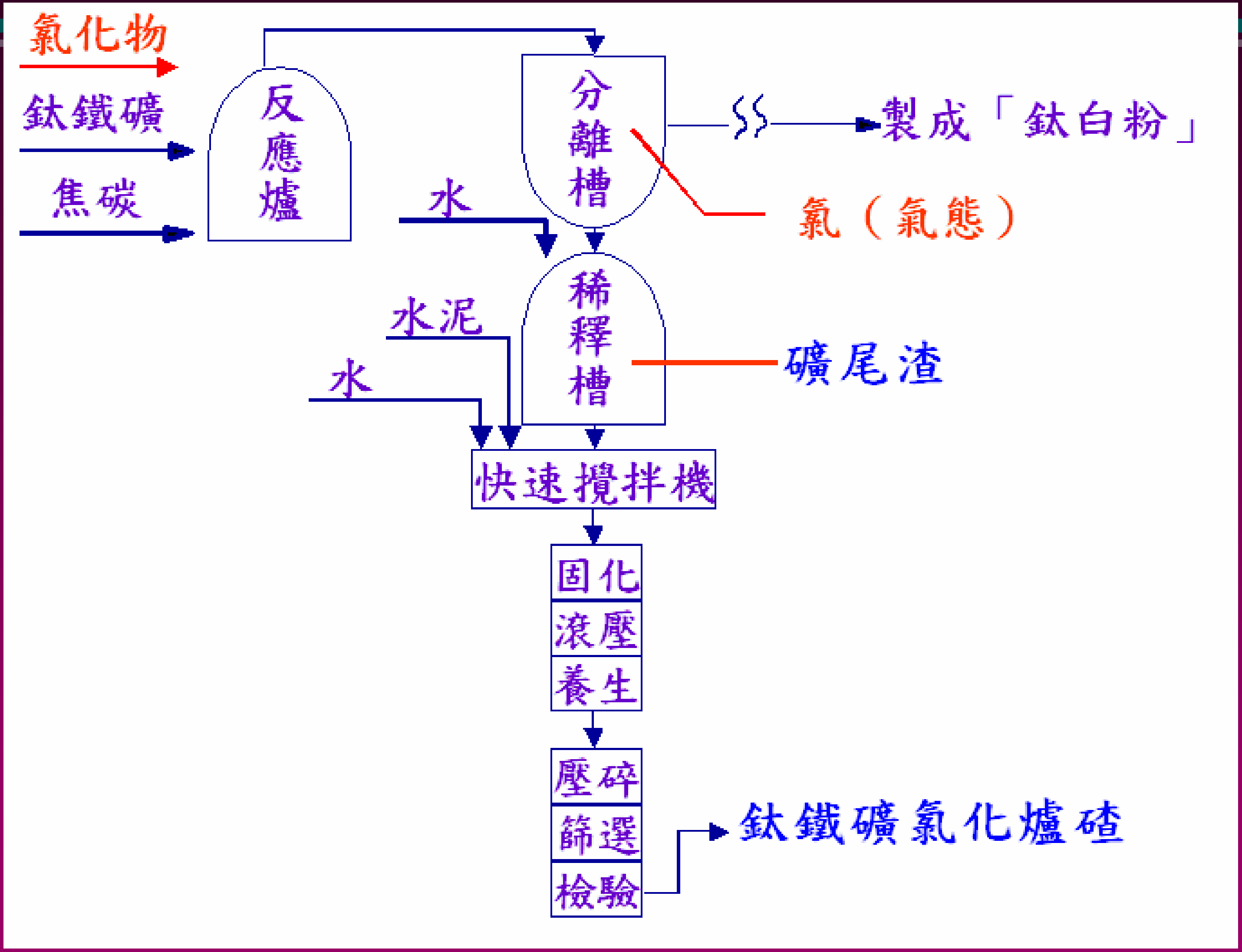
二氧化鈦製程及礦尾渣來源

- 礦尾渣是杜邦公司生產二氧化鈦而衍生的工業副產物，二氧化鈦又名氧化鈦或鈦白，俗稱鈦白粉。
- 製造鈦白粉分為硫酸法和氯化法二種方法。前者始於1916年，其製法是以濃硫酸150~220℃分解含鈦原料鈦鐵礦或鈦熔渣，將此硫酸鹽溶液水解，得到較純的$TiO_2 \cdot 2H_2O$沉澱物再予純化即得。由於其製程中所衍生的廢棄物及污染問題較嚴重，且有廢硫酸的產生，因而不建議使用。

文 獻 回 顧

- 氯化法是將鈦鐵礦、天然或合成金紅石及鈦熔渣在800℃的氯化爐中通氯進行氯化反應，得到的四氯化鈦在900~1,400℃的溫度下燃燒成為二氧化鈦。

鈦鐵礦氯化爐碴製造流程



製 作 流 程

- 製作過程是由氣態氯經由水冷凝後生成鹽酸（HCl），鹽酸即是由氫氧根加上氯離子聚合而成，其化學式：

$2FeTiO_3+7Cl_2+3C \rightarrow 2TiCl_4+2FeCl_3+3CO_2$

$TiCl_4 \rightarrow TiO_2+2Cl_2$

$Cl_2+H_2O \rightarrow 2HCl+\frac{1}{2}O_2\uparrow$

$HCl \rightarrow H^{+}+Cl^{-}$

- **礦尾渣特性**
- 礦尾渣是由天然鈦鐵礦提煉出二氧化鈦後，所產生之工業副產物，為深綠色膠體溶液，溶液中微細顆粒約佔35～45％，含氯化鐵、酸性及與鹼性物質反應會放出大量熱等。

溶解度的觀念

- 在一定溫度下，定量溶劑所能溶解溶質的最大量，稱為該溶質在該溶劑中的溶解度（Solubility），溫度改變時會產生不同的溶解度，常用莫爾濃度（M）來表示其溶解度之大小。一般對溶解度大於0.1M者，稱為可溶（Soluble）；溶解度小於0.1M者稱為微溶（Slightly Soluble）；而溶解度小於0.001M者，稱為極微溶（Very Slightly Soluble）；若溶解度極小者，稱為難溶或不溶（Difficult or Negligible Solubility）。

溶解度的影響因素

- （一）物質的本性：

  溶劑與溶質的性質若相近，則其溶解度甚大，若兩者性質不同，則溶解度甚小，即溶解的法則是性質相似者互溶(like dissolves like)。

- （二）壓力：

  固體或液體的溶解度受壓力的影響甚微，可以忽略。但壓力對氣體的溶解度的影響甚大。

溶解度的影響因素

- (三) 溫度：

許多物質溶於溶劑中有熱效應，稱為溶解熱(Heat of Solution)，少數為放出大量的熱，大部分為吸收熱量。若為放熱反應，則溫度升高，其溶解度反而減少，如$CaSO_4$、CaO、$CaCl_2$、Na_2SO_4等。若為吸熱反應，則溶解度增加，如KNO_3、$Pb(NO_3)_2$、$K_2Cr_2O_7$等，而NaCl其溶解熱很小(0.9kcal/mole)，故溶解度甚小。

沉澱之洗滌

- 張氏（1995）指出沉澱物之洗滌方式，單次大量洗滌液的洗滌方式，不如多次少量洗滌液的洗滌方法。
  - 膠體混凝理論

一般而言混凝係添加混凝劑於原水中，利用快混（Rapid Mixing）使混凝劑迅速且均勻分佈，增加其與膠體粒子間之碰撞機會，並破壞膠體粒子的穩定性。而膠凝是使不穩定之膠體粒子，藉由慢混（Slow Mixing）之方式，而逐漸形成微細膠羽，並利用速度坡降（Velocity Gradient）使其彼此間相互碰撞，而產生較大膠羽，以達到足夠之沉降速度。

混凝機理

1. 電雙層擠壓（Double-Layer Compression）
2. 吸附及電性中和（Adsorption and Charge Neutralization）
3. 沉澱絆除（Enmeshment in a Precitation）
4. 吸附與架橋作用（Adsorption and Interparticle Bridging）

膠體作用力

- 指很小之粒子（Particles）分散於某種介質(Medium) 而所構成的溶液稱為膠體溶液(Colloidal Solution)。

由Derjarguin, Landau, Verwey與Overbeek四位物理化學家所提出，通稱為DLVO模型，存在於膠體之間，造成小於數μm膠體穩定或聚集而固液分離的顆粒間作用力（Inter-Particle Forces）稱之為膠體作用力（Colloid Interactions）。

Gregory(1993)重新整理出膠體作用力

1. 凡得瓦爾力（Van Der Waals Interaction）
2. 靜電作用力（Electrical Interaction）
3. 水合效應（Hydration Effect）
4. 疏水性作用力（Hydrophobic Interaction）
5. 聚合物架橋（Polymer Bridging）
6. 組合作用力－膠體穩定性（Combined Interaction-Colloid Stability）

混凝劑種類

- 混凝劑種類之選擇以pH適用範圍廣、適用各種水質、混凝時間短、膠羽沉降性佳、價廉、對其他處理單元無不良影響為主要選擇因素。
- 污水處理之混凝劑

硫酸鋁（$Al_2(SO_4)_3 \cdot 18H_2O$）、多元氯化鋁、鋁酸鈉（$NaAlO_2$）、氯化鐵（$FeCl_3 \cdot 6H_2O$）、硫酸鐵（$Fe_2(SO_4)_3$）、硫酸亞鐵（$FeSO_4 \cdot 7H_2O$）等。大致上又可區分為聚合性（多元氯化鋁、多元硫酸鐵）與單核性（硫酸鋁、氯化鐵）。

濾材及過濾助劑之選擇

- 固液分離程序在化工程序中佔有重要的角色，在食品、礦業、醫藥、生化、污染防治等工業裡或現代生活中也是很重要的程序，一般分離程序可區分為：過濾、離心及分離、擴散、逆滲透、表面分離、吸附、離子交換、溶劑萃取等。過濾操作主要特點是可利用各種機械設備將固體物自流體中分離的一種程序，其主目的為：

  1. 減量化：污泥經適當處理後體積減少，相對地減少最終處置費，例如：清理費、搬運費、焚化、固化及掩埋費等。

  2. 安定化：確保污泥經適當處理後，不會形成二次公害。

  3. 回收汙泥中有用物質。

過濾器及濾材的種類和特性

- 濾器是達成固液分離的設備，製程上因處理量不同、流體性質不同、或要求的濾液之品質及濾餅的含液量之不同而有各式各樣的過濾裝置，下表列舉了一般常見的過濾器。

操作方式	過濾器種類
批次操作	板框式壓濾器
	葉濾器
	淺盤式過濾器
	槽型真空過濾器
半連續式操作	迴轉盤式過濾器
	帶狀壓濾機
	全自動壓濾機
連續式操作	迴轉圓筒式真空或壓力過濾器
	迴轉圓盤式真空過濾器
	帶狀真空式過濾器
	迴轉連續壓濾機

濾材種類

- 濾材是過濾器之心臟，其定義為「過濾程序中任何具多孔性且可使粒子（固體/液體）沉積於其表面或空隙間的物質」。下表列舉一般的濾材種類及其最小阻截粒徑。

	型式	濾材種類	最小阻礙粒徑
1	硬質濾材	平板濾網	100
2	金屬濾材	金屬網材	5
3	多孔性濾材	陶瓷/石材	1
		碳	1
4	濾蕊	纖維紗	5
5	塑膠濾板	單纖維編織板	10
6	薄膜	高分子聚合物	< 0.1
7	編織纖維	搓揉紗	5
8	不織布	紙	5
		聚合物不織布	10
9	散狀性濾材	粉末	< 0.1

助濾劑之種類與特性

- 助濾劑為改善過濾速度慢、濾材快速阻塞或濾液的澄清度無法達到要求等難過濾現象，助濾劑之使用為考慮要項。助濾劑是一種微細粒狀物質，不可壓縮的硬質顆粒。最普遍使用之助濾劑有：矽藻土、珍珠岩、焦碳及飛灰等。它可形成多孔、易穿透之結構以阻截固體物，而使流體通過。助濾劑種類繁多，以下歸納工業上常用的助濾劑：

  1. 矽藻土
  2. 珍珠岩
  3. 石綿
  4. 纖維素
  5. 鋸屑

助濾劑之應用

- 助濾劑是於過濾前加入，以改變懸浮物的過濾性質，助濾劑會增加漿體中之固體濃度，可促使粒子產生架橋及產生結構密緻的濾餅。助濾劑亦會降低流量變化程度，不規則粒子及圓形粒子有較佳的架橋傾向。
- 一般助濾劑的添加量為漿中懸浮固體物的0.01%～4%（w/w），而實際的添加量只能從實驗來決定。

三、水洗設備與研究方法

- 試驗材料
- 礦尾渣(KYC2)

由杜邦廠生產線提供，未加水泥拌合處理之原料，下圖所示黏稠狀膠體、顏色呈深綠色、酸性含氯化鐵等特性，液體中含大量微細顆粒易產生沉澱現象。

試驗水

（一）一般水洗水：來自台灣自來水公司之自來水。

（二）地下水：取自中央大學土木材料試驗室之地下水。

項目	水中Cl^-含量(mg/L)	pH	Conductivity (μs/cm)	Salt (%)	TDS (g/L)
自來水	12	7.1	180	0.0	0.09
地下水	21	7.5	116	0.1	0.24

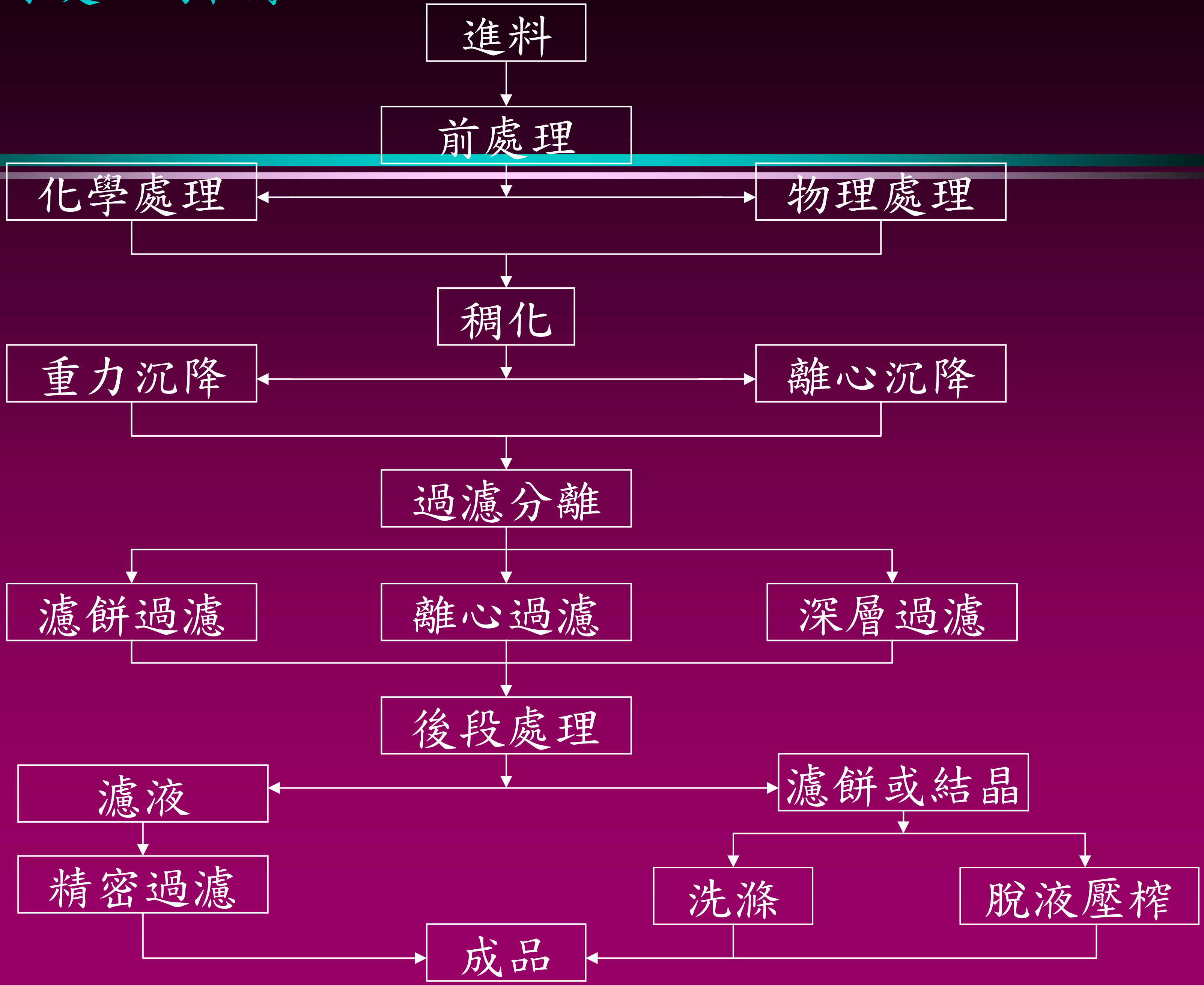
試驗用藥品

藥品名稱	等級	製造商
氫氧化鈉(NaOH)	分析級	日本島久藥品株式會社
石灰(CaO)	分析級	日本島久藥品株式會社
碳酸鈉($NaCO_3$)	分析級	日本島久藥品株式會社
硫酸鋁(Al_2SO_4)	分析級	日本島久藥品株式會社
矽藻土	分析級	日本小島化學藥品株式會社

試驗設備

設備名稱	廠牌/型號	用途	備註
烘箱	CHANNEL	烘乾爐碴材料	Max. 300℃
微量電子天平	METTLER AE200	調配藥品時秤重	±0.0001g
去離子水設備	MILLIPORE MILLI-Q	製造去離子水	R＞16MΩ
電動攪拌機	LB-101	攪拌爐碴材料	三段變速
真空過濾裝置	GAST	分離固液體	---------
真空幫浦	ROTARY VACUUM	抽真空	Max. 76cmHg
pH檢測計	JENCO MODEL 6173pH	量測試樣pH值	---------
離子層析儀	ASRS^{R}-ULTRA II-4mm (Dionex)	量測陰離子(Cl-)濃度	準確度：Conc.：±0.5%讀值

一般廢水處理的程序：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前處理
化學處理
物理處理
稠化
重力沉降
離心沉降
過濾分離
濾餅過濾
離心過濾
深層過濾
後段處理
濾液
濾餅或結晶
精密過濾
洗滌
脫液壓榨
成品

本研究流程圖：

收集文獻資料

↓

小規模水洗試驗

↓

氫氧化鈉、石灰 → 中和

↓

硫酸鋁 → 沉降

↓

碳酸鈉 → 加藥

↓

矽藻土 → 過濾

↓

量產型礦尾渣水洗試驗

↓

估算成本及結果分析

四、預期結果

- 本研究預期完成之具體成果如下：

1. 在小規模水洗試驗中，以氯離子含量分別在中和階段達到4000ppm，而水洗階段為500ppm的目標下，找出適當的水洗程序、方法與藥劑，期望在經濟和效率的條件下，可大量水洗礦尾渣。
2. 依試驗結果擬定大量水洗礦尾渣的程序，並量產KYC3，及盡量累積KYC3，以供後續研究使用。
3. 依試驗結果估算水洗礦尾渣的成本。

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dc.description.abstract	「礦尾渣」為杜邦公司工業生產衍生的副產品，與水泥拌合後凝結硬固成為「鈦鐵礦氯化爐碴」。目前鈦鐵礦氯化爐碴已再利用於道路基底層。其特性為經滾壓後有再膠結現象及含有大量氯離子，此試驗分別研究鈦鐵礦氯化爐碴再膠結的強度發展及水洗前處理礦尾渣。 試驗結果顯示，鈦鐵礦氯化爐碴經壓實後的抗壓強度或C.B.R.值，都有明顯隨齡期發展的趨勢。鈦鐵礦氯化爐碴有良好的體積穩定性，縱使在高溫狀態下或長期浸水膨脹率都符合並遠低於規範要求。 水洗前處理礦尾渣可有效降低水溶性氯離子含量。經由膠體沉降時間試驗結果發現，硫酸鋁及硫酸鐵其混凝效果較佳。添加碳酸鈉對水洗礦尾渣，能提高氯離子被溶出量，增加水洗成效。基本水洗（過濾）方式成效較佳。水洗後礦尾渣吸水率高於天然砂石甚多，所以水 泥礦尾渣砂漿流度值，會隨著高吸水率之礦尾渣用量增加而降低。 SCDS is one of the by-products produced by the DuPont Co., Ltd. After mixing with cement it is coagulated into TCS. Currently TCS is being adapted for pavement. It is re-glued and contained of a certain amount of chlorine ion. This experiment is aimed at the intensity of titanium iron chloride and the SCDS before water-wash. The result shows that the intensity and compression resisting or C.B.R. is enormously increasing with its sequence. TCS is very stable, it status is under the regulated standard even under high-temperature or after a long-time of soaking in water. Before the washing the SCDS, we can efficiently decrease the water chlorine ion. After the experiment of colloid subsiding, we found that aluminum sulfate and iron sulfate have better concrete result. Adding in calcium carbonate when washing SCDS can increase the chlorine ion's dissolving. Basic washing (filtering) approach is more effective. After washing, the SCDS absorbs much more water than regular sand. Therefore the flowing rate of concrete SCDS is increasing when the use of SCDS with high absorbing intensity's increasing.	en_US

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dc.publisher	國立中央大學圖書館	en_US
dc.subject	鈦鐵礦氯化爐碴,CBR,水洗,礦尾渣,water-wash,SCDS,TCS,CBR	en_US
dc.title	鈦鐵礦氯化爐碴應用於道路基底層及礦尾渣水洗前處理之研究 TCS applies to the pavement base or subbase course and in front of the SCDS water-wash research the processing	en_US
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水洗礦尾渣造粒後之粒料特性探討

Investigate Washed SCDS Made Aggregate Property

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中文摘要

礦尾渣為工業煉製二氧化鈦的副產品, 為顆粒細、氯含量高之酸性物質, 原以加2倍水泥造粒製成觀音石, 作為道路基底層級配料。為避免觀音石內部氯離子釋出所可能造成的金屬管路腐蝕問題, 本研究主要探討礦尾渣水洗除氯的程序、造粒的最佳配比、粒料的性質及CBR值等, 評估取代觀音石及放寬使用限制之可行性。
研究發現僅用清水清洗對礦尾渣內的氯離子去除量有一定極限, 若使用5%碳酸鈉水溶液, 才能增加礦尾渣內氯離子的溶出。利用壓濾機清洗可達到氯離子殘留量在500 ppm以下。結果又發現試體的濕密度值為影響造粒強度的關鍵因素, 當以水灰比0.4, 水泥/濾餅比為 1.2或1.6造粒(簡稱KYC III), 養護7天的強度可達目標強度210 kgf/cm2;KYC III篩分析結果符合第二類型基層級配料要求, 由CBR值顯示KYC III經養護28天後, 適用於道路基底層材料。

英文摘要

The sludge is a by-product in the industry of titanium dioxide refinement i.e., SCDS . It is a kind of acidic material of fine granular particles with high chloride ion content. The SCDS is originally used for making granulized by mixing with two-fold cement to serve as the aggregate i.e., TCS base course material for the foundation of road pavement .This study, to avoid the problems of corrosion on embedded metallic pipelines resulted form chloride ion released form inside of TCS, discussed the procedure of removing chloride ion form SCDS by water washing, the proportioning for TCS granulation, the properties of TCS materials, the California Bearining Ration i.e., CBR value of TCS materials and so on. In addition, the feasibility assessment of replacing the traditional manufacturing procedure oh TCS and loosening the restrictions on the use of TCS had also been conducted.
Results showed that the SCDS was still full of chlorine ion after being water-washed. Only if 5% soda ash was used could the chlorine ion be released from SCDS. Additionally, the use of filtering machine allowed the residual of chlorine ion in SCDS less than 500 ppm. Another finding was that the humidity and density were the determinants of strength for TCS. When being mixed with the proportion of 0.4 w/c and 1.2 or 1.6 cement (i.e., KYC) for 7 days, the strength of TCS could reach 210 kgf/cm2.

Committee

指導教授 - 李 釗

Keywords

TCS
Chloride ion
KYCIII
SCDS
觀音石
礦尾渣
KYC III
氯離子